MODELLING THE ADSORPTION OF CYANOGEN CHLORIDE (CNCl): A FIRST STEP TOWARDS ITS REPLACEMENT AS A MILITARY TESTING AGENT

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Introduction

Cyanogen chloride is one of the most commonly used test gases for activated carbon filters for protection against chemical warfare agents. This is due to the high volatility and high toxicity of CNCl that is not well retained by classical activated carbon despite the wide use of activated charcoals in air purification. In order to improve the efficiency of activated cabon towards small molecules with low boiling points, it is impregnated with metal salts that promote chemisorption on the carbon surface. The better way to validate the impregnation process, is to test the performance of the impregnated carbon against CNCl.

However, due to international legislation about chemical weapons, the production, transport and use of CNCl are strictly controlled and restricted. Testing laboratories are therefore looking for a replacement agent. In the past, research was focussed on the very specific interactions between CNCl and the metal complexes dispersed on the surface. In our approach we try to model the adsorption behaviour by a sensitivity analysis, looking at the influence of several parameters, both environmental and coal based. The ultimate goal being to find another gas that presents a similar macroscopic behaviour, i.e. that gives analogous results for critical properties (adsorption capacity or breakthrough time) and whose adsorption is affected by water to the same extent as CNCl.

The Wheeler-Jonas equation is a well-known predictive equation for calculating breakthrough times of physisorbed organic vapours on activated carbon beds. Recently, the authors of this article have successfully extended the scope of applicability of the equation to other vapours such as chlorine[1] and ammonia[2] which are typically chemisorbed. Earlier in the past, the application of the Wheeler-Jonas equation to CNCl adsorption has been advanced by Staginnus[3].

In this work, as a first step, we want to investigate the applicability of the Wheeler-Jonas equation to the CNCl adsorption.

Experimental

Breakthrough tests have been carried out on beds of two different activated carbons. The first one is a Whetlerite carbon ASCT (Chemviron Carbon) that is impregnated with Cu-Cr salts for their interactions with CNCl and HCN and triethylenediamine ($C_6H_{12}N_2$) for his protection afforded to the Cu-Cr complexes against the ageing process (destruction of the active Cu-Cr species in presence of adsorbed water vapor). The second charcoal is a BPL carbon that is the parent (non-impregnated) carbon of ASCT.

Different parameters have been varied : the volumetric flow rate, the inlet concentration and the weight of the AC bed. The relative humidity (RH) for the pre-wetting of the carbon bed and the humidity of the air stream were either 0% or 80%. The breakthrough concentration has been fixed to 2.5 mg/m³. Tests were perfomed at 293 ± 3 K. The diameter of the filter cartridge was 9 cm. The Dubinin-Radushkevich micropores volumes as determined by N_2 adsorption are 0.48 cm³/g for BPL and 0.31 cm³/g for ASCT.

Theoretical

<u>CNCl adsorption</u>

The adsorption of CNCl on Cu-Cr impregnated carbon consists in a decomposition of the CNCl molecule whose mechanism has not been clearly elucidated up to now and is very complex. One of the reasons for the great difficulty to understand the adsorption mechanism is the very complex nature of the surface composition of ASC impregnated whetlerite carbons[4,5,6,7]. The two-step nature of this decomposition is commonly accepted : first, physical adsorption takes place in the micropores, this is followed by chemical reactions with Cu^{II} and Cr^{VI} species[8,9]. Several reactions have been proposed for the decomposition of CNCl catalysed by the Cu-Cr supported salts[10,11] :

hydrolysis :	$CNCl + H_2O \rightarrow HOCN + HCl$
	$HOCN + H_2O \rightarrow NH_3 + CO_2$
redox reaction :	$CNCl + H_2O \rightarrow HOCl + HCN$
catalytic oxidation :	$2\ CNCl + 4\ [O] \rightarrow 2\ CO_2 + N_2 + Cl_2$

But it is commonly assumed that the adsorption proceeds according to the hydrolysis of CNCl ; consequently water is a pre-requisite for the reaction to occur efficiently.

<u>The Wheeler-Jonas equation</u>

The Wheeler-Jonas equation is a very simple tool to estimate breakthrough times of granular activated carbon beds requiring only macroscopic, easily available parameters :

$$t_b = \frac{W_e m}{Q C_{in}} - \frac{W_e \rho_b}{k_v C_{in}} \ln\left(\frac{C_{in} - C_{out}}{C_{out}}\right)$$

where t_b is the breakthrough time (min),
W_e the static adsorption capacity of the activated carbon (g/g),
m the mass of the carbon bed (g),
C_{in} the inlet concentration (g/l),
C_{out} the chosen breakthrough concentration (g/l),
Q the volumetric flowrate (l/min),
ρ_b the bulk density of the activated carbon (g/l)
and k_v the overall rate coefficient (min^{-1}).

The two unknown parameters in this equation are W_e and k_v. In the case of organic vapour adsorption, i.e. pure physisorption, W_e is normally estimated by means of the Dubinin-Radushkevich equation[12] and k_v can be calculated using a semi-empirical equation proposed by Wood and Lodewykx[13] :

$$k_v = 800.\beta^{0.33}.d_p^{-1.5}.v_L^{0.75}.\sqrt{\frac{W_e}{M}} \qquad (2)$$

where β is the similarity constant of the Dubinin-Radushkevich equation,
v_L the linear velocity through the carbon bed (cm/s),
d_p the mean diameter of the activated carbon particles (cm) ,
and M the molar weight of the vapour.

In the case of chemisorption, these two parameters cannot be calculated a priori and a set of experiments has to be performed. When Wheeler-Jonas is applicable to an adsorption process, plotting t_b versus the mass of the carbon bed should yield a straight line, allowing thereby to calcultate W_e and k_v. W_e is linked to the slope of the line and k_v to the intercept with the y-axis. To test the applicability of the Wheeler-Jonas equation, one has to perform a number of breakthrough experiments to verify if the underlying relations of Eq.1 are fullfilled.

Results and discusion

Influence of humidity

Some breakthrough tests were performed under 3 different humidity conditions :

- on as-received carbons with dry air ;
- on as-received carbons with humid air at 80 % RH ;
- on pre-conditionned carbons at 80% RH with humid air at 80 % RH .

Tables 1 and 2 present the breakthrough times (t_b) for ASCT and BPL carbons respectively. From the t_b results, it is straightforward that humidity plays a different role in the CNCl adsorption on ASCT and BPL : on ASCT, humidity enhances the adsorption capacity but on BPL it has an adverse affect and the longer t_b are measured in completely dry conditions. This observation is consistent with an adsorption mechanism on ASCT involving water whereas on BPL water is in competition with CNCl for pure physisorption in the micropore volume as it would be the case for an organic vapour.

This supports the idea of the physisorption of CNCl on BPL as it has been demonstrated previously[14].

Table 1: CNCl breakthrough experiments results for ASCT under different test conditions

m AC (g)	pre-cond. RH (%)	air stream RH (%)	Q (l/min)	C_{in} (g/m³)	t_b (min)
50	0	0	30	2	4
75	0	0	30	2	33
100	0	0	30	2	58
125	0	0	30	2	112
150	0	0	30	2	150
75	0	0	15	2	103
75	0	0	20	2	43
75	0	0	30	2	33
75	0	0	40	2	8
75	0	0	60	2	6
75	0	0	30	1	106
75	0	0	30	2	33
75	0	0	30	3	12
75	0	0	30	4	12
75	0	80	30	2	57
100	0	80	30	2	128
125	0	80	30	2	226
125	0	0	30	2	112
125	0	80	30	2	226
125	80	80	30	2	185

RH = relative humidity
outlet concentration = 2.5 mg/m³, diameter of filter bed = 9 cm

Table 2: CNCl breakthrough experiments results for BPL under different test conditions

m AC (g)	pre-cond. RH (%)	air stream RH (%)	Q (l/min)	C_{in} (g/m³)	t_b (min)
125	0	0	30	2	53
125	0	80	30	2	20
125	80	80	30	2	< 15*
125	80	0	30	2	31

* could not be measured correctly

As we compare the breakthrough times for ASCT and BPL under complete dry conditions, ASCT still provides better performances than BPL (about two times longer).

Apparently residual humidity on the carbon or in the air (RH_{air} ≤10%) is sufficient to permit chemisorption on ASCT. This type of behavior is in contradiction with the results previously reported on Cl_2 adsorption where humidity did not seem to influence breakthrough times[1].

Applicability of the Wheeler-Jonas equation

As we plot the breakthrough times versus the weight of the carbon bed for ASCT (Fig. 1), we obtain a straight line which is a first indication towards the applicability of the Wheeler-Jonas equation to the CNCl adsorption.

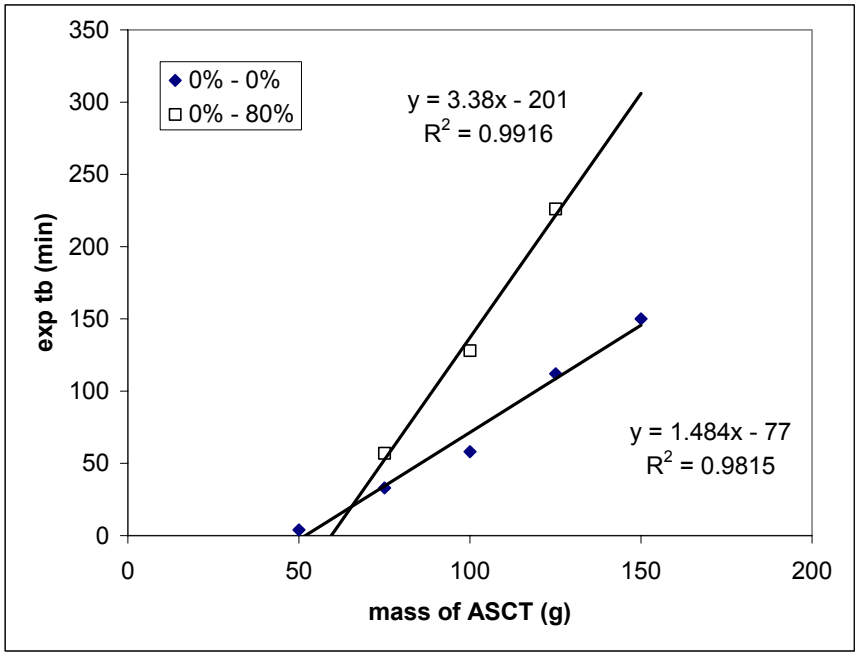

Fig. 1 : plot of the breakthrough times (t_b) in function of the carbon bed weight for ASCT in complete dry conditionds (♦) and with a humid air stream (80% RH) (➙) (Q = 30 l/min ; C_{in} = 2g/m³)

Using the slope, we have calculated for W_e a value of W_e = 0.089 g/g for dry ASCT tested with dry air (0%-0%) and a value of W_e = 0.203 g/g for dry ASCT tested with a humid air stream of 80% RH (0%-80%). The adsorption capacity of ASCT is higher under humid conditions than under dry conditions as could be expected from the higher breakthrough times.
The values calculated for ASCT for the rate coefficients from the intercept with the y-axis are 2260 and 2023 min^{-1} respectively for (0%-0%) and (0%-80%) conditions.

Theortical k_v values can be calculated with the empirical formula of Wood-Lodewyckx (eq. 2) taking for β the value of 0.64[15] and for W_e the values calculated above. This value of 0.64 for β has been found for CNCl on BPL.

Table 3 : experimental vs calculated k_v values for CNCl adsorption on ASCT

RH	k_v calc from eqn 2 (min^{-1})	k_v exp (min^{-1})
0% - 0%	2980	2260
0% - 80%	4480	2023

If theoritical k_v values are higher than experimental values in both cases, the difference is much larger in humid conditions than in dry ones. This arises from the fact that the W_e value used here to calculate k_v is much higher than for pure physisorption. The k_v experimental values seem to indicate that the rate controlling step is the same under both humid and dry conditions, suggesting a rate controlling step bound to the CNCl transport from the gas phase to the reaction sites rather than to the chemical reactions responsible of the CNCl decomposition. Under dry conditions, where the proportion of physisorption in the overall CNCl removal process is greater, the calculated k_v value is close to the experimental value. This is a situation close to what was found for NH_3 and Cl_2 where it has been shown that the surface diffusion is the rate controlling step.

With the experimental values of W_e and k_v found above it is now possible to calculate breakthrough times for ASCT in equivalent humidity conditions but for other carbon weights, inlet concentrations or other air flows, i.e. extrapollating laboratories results to other environmental conditions. Comparaison between experimental and calculated values is illustrated in Fig. 2.

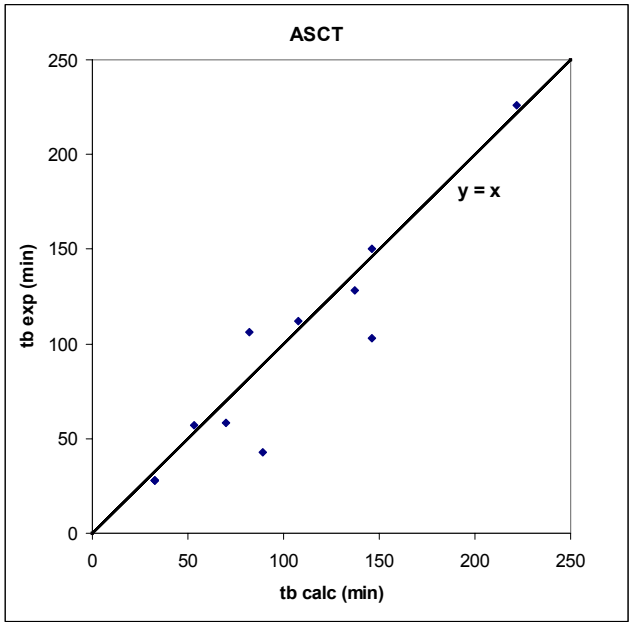

Fig 2 : Comparaison between experimental and calculated breakthrough times for ASCT for different experimental conditions

As one can see, the Wheeler-Jonas equation can predict quite well the breakthrough times for CNCl adsorption on ASCT. The least satisfactory results are found when the air flow is varied. More experimental results have to be collected to validate this assumption, in particulary under humid conditions.

Conclusions

The preliminary results presented here prove the utility of the Wheeler-Jonas equation for the CNCl adsorption even if the parameters W_e and k_v cannot be determined theoretically : some prior experiments have to be done before using Wheeler-Jonas for extrapollating t_b to other test conditions (Q, C_{in}, m) but in the same environmental circumstances (RH and T).

However more experimental work has to be done to verify the relation between the air flow and t_b and to validate the assumption that the Wheeler-Jonas equation is well applicable to CNCl adsorption. If this work gives a first insight on the overall macroscopic process, the study of some particular aspects of the CNCl adsorption would help in his modelling:

- The influence of humidity has to be precised by varying the air stream humidity
- The carbon capacity, W_e, and the rate coefficient, k_v, should be determined for BPL where only pure physisorption occurs.
- The calculated value for W_e should be linked to physico-chemical properties of the carbon such as the Cu-Cr coverage.
- It should be verified that k_v is always linked to the surface diffusion for different inlet concentrations.

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